GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: June 16, 1980

Project Title: A Study of the Reaction of OH with ClO

Project No: A-2660

Project Director: Dr. A. R. Ravishankara

Sponsor: Chemical Manufacturers Association, Inc.; Washington, D.C. 20009

Agreement Period: From May 23, 1980 Until ~~May 22, 1981~~ 2/28/82 ~~3/31/81~~ (R&D Per. Period)

Type Agreement: CMA Reference No. FC 80-295-Part II

Amount: $43,007

Reports Required: Quarterly Progress Reports: Final Report

Sponsor Contact Person (s):

Technical Matters

Dr. Joseph M. Steed
E.I. du Pont de Nemours & Co., Inc.
Experimental Station 356/345
Wilmington, Delaware 19898

(302) 772-2700

Contractual Matters
(thru OCA)

Mr. John C. Van Horn
Project Administrator
Fluorocarbon Research
Chemical Manufacturers Association
1825 Connecticut Avenue, N.W.
Washington, D. C. 20009

(202) 328-4200

Defense Priority Rating: None

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GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF CONTRACT ADMINISTRATION

SPONSORED PROJECT TERMINATION SHEET

Date 8/6/82

Project Title: A Study of the Reaction of OH with ClO

Project No: A-2660

Project Director: Dr. Ravishankara

Sponsor: CMA

Effective Termination Date: 11/30/81

Clearance of Accounting Charges: 2/28/82

Grant/Contract Closeout Actions Remaining:

- [x] Final Invoice ~~and Closing Documents~~
- [ ] Final Fiscal Report
- [x] Final Report of Inventions (positive only)
- [x] Govt. Property Inventory & Related Certificate
- [ ] Classified Material Certificate
- [ ] Other _____

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FORM OCA 10:781

First Quarter Report

A STUDY OF THE REACTION OF OH WITH ClO

August 20, 1980

During the first three months, most of the time has been spent on acquiring necessary equipment, i.e., flow meters and a microwave power supply, and supplies.

A new flow tube (1" I.D.) is being fabricated to replace our old flow tube (2" I.D.). The rest of the system is being assembled.

Essentially no manpower has been spent on this project during this quarter. As was indicated before initiation of the contract, the Principal Investigator was out of the country for 5 weeks and hence no experiments have been carried out.

Anticipated Work During the Next Quarter:

1) Complete assembly of equipment
2) Start room temperature measurement of the rate constant for the reaction.

NOTE: The carcinotron (the microwave source) is out on repair and is expected to be back this quarter so that the interferometer would be operational in the next 4 months.

A-2660

2nd PROGRESS REPORT FOR CMA PROJECT (A-2660)

During the last two months, the assembly of the discharge flow tube apparatus was completed. The OH resonance fluorescence detection system has been optimized. To ensure proper operation of the flow tube (i.e., minimal OH wall loss, lack of wall chemistry, flow meter calibrations, etc.), we measured the rate coefficient for the reaction,

$$OH + HCl \rightarrow H_2O + Cl,$$

at 298K. The OH decay rates were exponential and the measured rate coefficient agrees well with previous measurements.

The study of OH with ClO has begun. It is expected that the 298K value will be measured in the next two months. The temperature dependence study will begin soon after the room temperature measurements are completed.

A-2660

Third Quarter Progress Report

A STUDY OF THE REACTION OF OH WITH ClO

A-2660

Period Covered: December 1980 - February 1981

Ref. No. FC 80-295-Part II

Prepared for:

Chemical Manufacturer's Association
1825 Connecticut Avenue, NW
Washington, D.C. 20009

Attention: Dr. John Van Horn

By:

Molecular Sciences Branch
Physical Sciences Division
Electromagnetics Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Contracting through:

Georgia Tech Research Institute
Atlanta, Georgia 30332

Project Director:

A.R. Ravishankara

February 19, 1981

THIRD QUARTER PROGRESS REPORT
December 1980 - February 1981

Project A-2660

The kinetics of the reaction of OH with ClO,

$$OH + ClO \xrightarrow{k_1} \text{Products} \qquad (1)$$

was studied as a function of temperature using a discharge flow apparatus. The flow tube was equipped with a movable injector and a fixed injector to facilitate introduction of various species. OH radicals were prepared (upstream of the movable injector) in the flow tube itself by titrating H atoms (introduced via the fixed injector) with NO_2,

$$H + NO_2 \rightarrow OH + NO \quad . \qquad (2)$$

[OH] was measured using resonance fluorescence detection.

ClO radicals were prepared by adding O_3 to a stream of He containing Cl atoms in the movable injector,

$$Cl + O_3 \rightarrow ClO + O_2 \quad . \qquad (3)$$

To ensure that Cl atoms were in a large excess over added O_3 the chemiluminescence due to the recombination of Cl atoms was monitored with a red sensitive PM tube. The length of the movable injector ($\sim$ 120 cm) was sufficient to ensure thermalization of all ClO before they entered the main flow tube.

All flows were measured using calibrated electronic mass flow meters and the pressure was measured using an MKS capacitance manometer. All

experiments were carried out at ∿ 2 Torr of He. Concentrations of O_3 and NO_2 were measured by using UV absorption at 254 and 366 nm, respectively.

Pseudo-first order conditions, with [ClO] >> [OH], were maintained throughout the course of this work. k_1 was measured by two methods: (1) OH concentration was measured at various ClO concentrations at a fixed reaction distance—a plot of $\ell n \frac{[OH]_o}{[OH]}$ vs. [ClO] yields k_1, (2) $\ell n \frac{[OH]_o}{[OH]}$ was measured at a set [ClO] as a function of distance to obtain $k' \equiv k_1[ClO]$. Then, k' was measured as a function of [ClO] to extract k_1.

To ensure that no secondary reactions were affecting our measurements, $[OH]_o$ and [ClO] were varied over a wide range. The presence of excess Cl atoms ensured that any HO_2 radicals produced in Reaction (1) were removed via its reaction with Cl (to yield HCl) rather than with NO (to yield OH).

Table I lists measured values of k_1 as a function of temperature. A fit of our data to an Arrhenius expression yields,

$$k_1 = (4.9 \pm 3.6) \times 10^{-12} \exp[(1.8 \pm 2.0) \times 10^2/T] \text{ cm}^3\text{molec}^{-1}\text{s}^{-1} .$$

However, we prefer to report a temperature independent value,

$$k_1 = (9.6 \pm 2.5) \times 10^{-12} \text{ cm}^3\text{molec}^{-1}\text{s}^{-1}, \text{ for } 248 < T < 335 \text{ K},$$

since the calculated overall errors at each temperature are nearly 20%.

Currently, the Michelson interferometer is being interfaced with the discharge flow tube. During the coming months this apparatus will be used to measure the yield of HCl in Reaction (1). These measurememts will be carried out at 298 K. If a significant yield of HCl is measured at 298 K, then HCl yield at stratospheric temperatures will be investigated.

A-2660

Georgia Institute of Technology
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

May 26, 1981

Dr. John C. Van Horn
Project Administrator
Fluorocarbon Research
Chemical Manufacturers Association
1825 Connecticut Avenue, NW
Washington, DC 20009

Dear Dr. Van Horn:

Enclosed is a copy of the Bimonthly Progress Report entitled "A Study of the Reaction of OH with ClO".

If you have any questions, please call me.

Sincerely,

A.R. Ravishankara

ml

BIMONTHLY PROGRESS REPORT

A-2660

SUBMILLIMETER WAVE INVESTIGATION OF MOLECULAR CONCENTRATIONS

The semi-confocal Fabry-Perot interferometer for observations on HCl at 625 GHz has been constructed. Efforts are currently underway to generate the coherent signal by harmonic generation from either a mm klystron or a 312.5 GHz carcinotron. The most appropriate generation scheme is to employ the klystron as the driving source for the harmonic generator. This will provide a means for excitation with a frequency-stable source, since the klystrons are readily phase-locked to a frequency standard. A survey of available klystrons has resulted in the use of an OKI 90V11 oscillating at ~89.3 GHz. The seventh harmonic of this tube will provide the desired frequency for HCl.

Schottky barrier diodes are employed as harmonic generators and detectors. Initial observations have resulted in generation of signals to 357 GHz, and further work on the generators is currently being performed. Improvement in the generator should achieve the necessary seventh harmonic.

The repair of the 300 GHz carcinotron power supply has been completed, and the supply is due to be shipped. The use of this source will allow us to double to the frequency of HCl or to provide superheterodyne detection of the power generated by the klystron.

During the next reporting period, it is projected that the power will be generated at 625 GHz, the interferometer will be tested and observations performed on HCl.

A-2660

Progress Report

A STUDY OF THE REACTION OF OH WITH ClO

Performance Period: May 23, 1981 to November 22, 1981

A-2660

February 8, 1982

During this period further attempts were made to obtain and maintain the needed microwave frequency to detect HCl. Unfortunately, due to equipment failure the HCl could not be detected.

A-2660

A STUDY OF THE REACTION OF OH WITH ClO

By

A. R. Ravishankara

OTHER INVESTIGATORS

F. L. Eisele
P. H. Wine
J. J. Gallagher
V. Brady

Electromagnetics Laboratory
Engineering Experiment Station
Georgia Institute of Technology
Atlanta, Georgia 30332

Prepared for:

Chemicals Manufacturers Association
2501 M Street, N.W.
Washington, D.C. 20037

FINAL TECHNICAL REPORT

TABLE OF CONTENTS

Abstract

The technique of discharge flow-OH resonance fluoresce was used to study the kinetics of the reaction of OH with ClO. The rate coefficient for this reaction, k_1, was measured over the temperature range 248-355K by following the concentration of OH in excess ClO (under pseudo-first order conditions). It was discovered that the reaction of Cl atoms with HO_2 reaction product yielding OH resulted in the underestimation of k_1 and the obtained results were appropriately corrected. k_1 was found to be nearly independent of temperature with a mean value of $(1.17 \pm 0.33) \times 10^{-11}$ $cm^3 molecule^{-1} s^{-1}$. The obtained results are compared with those from previous measurements. This work is described in Chapter I.

The product, HCl, which could be formed in reaction (1) was to be measured using submillimeter wave spectroscopy. Due to difficulties encountered in the generation of the need frequency of 625 GHz, the experiments could not be carried out. The theory behind this technique and a description of the efforts that were carried out are described in Chapter II.

Chapter I

THE KINETICS OF THE REACTION OF OH WITH ClO

A. R. Ravishankara

F. L. Eisele

P. H. Wine

Introduction

OH and ClO are two very important radical species in the stratosphere. OH engages in many ozone destruction cycles as well as reactions which convert inactive species to active species (example, $OH + HCl \rightarrow H_2O + Cl$) and active species into inactive or less active species (example, $OH + NO_2+M \rightarrow HNO_3+M$, and $OH + HO_2 \rightarrow H_2O + O_2$). Similarly, ClO engages in ozone destruction cycles as well as other reactions which control the concentration of many reactive radical species. The reaction of OH with ClO,

$$OH + ClO \rightarrow HO_2 + Cl \qquad (1a)$$

$$\rightarrow HCl + O_2 \qquad (1b)$$

is of interest since this reaction has the potential for being a sink for both OH and ClO, if the branching ratio for reaction (1b) is large. Furthermore, predicted ratios of HO_2 to OH and ClO to Cl depend upon both the rate constant and branching ratio for reaction (1). Since calculated stratospheric ozone perturbations depend upon both $[HO_2]$ / [OH] and [ClO]/[Cl], it is important to characterize reaction (1) as completely as possible.

Leu and Lin[1] measured the net rate coefficient, $k_1 = k_{1a} + k_{1b}$, at 298K to be $(9.1 \pm 1.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} using a discharge flow tube. In addition, they estimated the upper limit for the branching ratio, k_{1b}/k_1, to be 35%. To verify the results of Leu and Lin at 298K and to obtain the value of k_1 at stratospheric temperatures, we have measured k_1 as a function of temperature using a discharge flow - OH resonance fluorescence apparatus. The results of this investigation are presented here.

Experimental

A discharge flow apparatus, shown in Figure 1, was used to study the kinetics of reaction (1). The concentration of OH was monitored as a function of reaction time in excess ClO using resonance fluorescence detection. Since this condition ensured pseudo-first order kinetics in OH, the only species whose absolute concentration had to be known was ClO. The ClO concentration was assumed to be equal to the measured concentration of O_3 added to an excess of Cl atoms since reaction with Cl rapidly and quantitatively converts O_3 to ClO. ClO was introduced into a flow tube (1" i.d.) via a (3/8" o.d.) movable injector while OH was prepared in the main body of the flow tube via the standard technique of H atom titration with NO_2:

$$H + NO_2 \rightarrow OH + NO. \qquad (2)$$

H atoms were produced via a microwave discharge of a small amount of H_2 in He. The flow tube was coated with halocarbon wax to decrease the wall loss of OH.

The detector section of the flow tube consisted of a 2.6 cm diameter brass tube whose inside was coated with FEP teflon and overcoated with halocarbon wax. This tube was connected to the glass flow tube using Viton o-rings on one side and to a pump through a large glass trap on the other side. A thermocouple could be introduced from the pump end of the detector section into the flow tube such that the gas temperature in the flow tube could be directly measured. The detector section had 8 ports, two sets of four each. The first set of four was used for resonance

fluorescence detection of OH. The output of OH resonance lamp was collimated by a series of apertures and then focused on the opposite exit port into a light trap. The resonance fluorescence emission was collected at 90° to the incident beam by a 1" focal length quartz lens and then focused on to the photocathode of a photomultiplier tube (RCA 8850). A bandpass filter (center wavelength - 309 nm, FWHM - 10 nm) and a stack of visible cutoff filters (7-54) were placed between the PM tube and the lens to isolate emission due to OH ($A^2\Sigma(v=0) \rightarrow X^2\Pi(v=0)$]. The output of the photomultiplier tube was amplified and counted using a pulse counter. In preliminary experiments, it was determined that $\sim 5 \times 10^8$ OH/cm^3 could be detected with a S/N = 1 for a 1s integration. The second set of ports were used for monitoring Cl atoms via the chemiluminescent recombination reaction,

$$Cl + Cl \rightarrow Cl_2 + h\nu \ (\lambda > 500 \text{ nm}). \qquad (3)$$

The chemiluminescence was monitored using a red sensitive PM tube (Hamamatsu R928P) and a broadband red filter (OG-610). The output of the PM tube was measured by an electrometer.

All gas flows were controlled by needle valves and measured using calibrated mass flow meters. The diluent was added upstream of all other inlets in the flow tube. The pressure in the flow tube was measured in two places, upstream near the OH production region and downstream near the detector. There was very little difference in pressure between the two ports. All concentrations were calculated based on the measured mass flow rates, pressure in the flow tube, and the known concentrations in

the source mixtures. The concentration of O_3 and NO_2 in the source mixtures were measured by absorption at 253.7 nm and 365 nm, respectively. These concentrations were known to better than 5% accuracy. The Cl_2 source mixture was prepared manometrically while a 0.1% H_2/He mixture was purchased from Matheson gas products.

All gases except O_3 were obtained from Matheson gas products and had the following stated purity levels: He > 99.9995%, Cl_2 > 99.96 %, H_2> 99.9995%, NO_2 > 99.5%. O_3 was prepared by using an ozonizer and stored on silica gel at 197°K. Before use, O_3 was liquified in a bulb at 77°K and all O_2 pumped out. NO_2 was mixed with excess high purity O_2 to convert NO into NO_2 and then O_2 was pumped away while freezing NO_2 at 197°K. Cl_2 was degassed before use.

The discharge flow tube was tightly wrapped with copper tubing and then covered with thermally insulating material. By circulating hot or cold fluids from temperature controlled baths through the copper coils, the temperature in the flow tube was controlled to within $\pm$ 1°K. The temperature of the gas in the flow tube was measured just before and just after the experiments. The detector section was always maintained at room temperature.

Since the flow tube apparatus was newly assembled and "untested," we used it to measure the well known rate coefficient[2] for the reaction

$$OH + HCl \xrightarrow{k_4} H_2O + Cl . \qquad (4)$$

Our measured value of k_4 agreed with the evaluated results[2] to within 10%

at both 298°K (7.1×10^{-13} cm^3 $molecule^{-1}s^{-1}$) and 248°K (5.1×10^{-13} cm^3 $molecule^{-1}s^{-1}$). This close agreement suggests the lack of any major systematic errors in the apparatus.

Before investigating the reaction of OH with ClO, it was necessary to measure the rate coefficients for the reactions of OH with Cl_2 and Cl.

$$OH + Cl_2 \rightarrow \text{Products} \qquad (5)$$

$$OH + Cl \rightarrow \text{Products} \qquad (6)$$

since both of these species were present in great excess over ClO. Reactions (5) and (6) were studied under pseudo-first order conditions with Cl_2 or Cl in excess over OH. The experimental procedure employed to carry out the measurements was the same as that for reaction (1) and is described below. It was found that k_5 was $\sim 7.4 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1} while $k_6 < 5 \times 10^{-14}$ cm^3 $molecule^{-1}s^{-1}$. In the case of k_6, the absolute concentration of Cl atoms was not known accurately and was estimated.

The experimental procedure employed to study reaction (1) was as follows: the flow tube was conditioned by flowing OH through it for approximately 10 minutes before measurements were made. The background resonance fluorescence counts were obtained by turning off the H atom discharge and compared with the signal obtained when H atom source was on and NO_2 not added to the tube. It was found that small amounts ($\sim$1% of the total) OH were produced even in the absence of added NO_2 due to either the discharge source or the reaction of H atoms with the walls. Once the background counts were measured, $\sim 5 - 10 \times 10^{10}$ OH cm^{-3} was generated and the signal measured. Then Cl_2 was added to the flow tube

the microwave discharge was turned on to convert Cl_2 to Cl atoms. As mentioned above, OH signal was not reduced due to reaction with either Cl or Cl_2. A known concentration of O_3 was added to the stream of Cl atoms, all the while making sure that there was an excess of Cl atoms as indicated by the chemiluminescence signal. The distance between the point of O_3 addition to Cl atoms and to the end of the injector was $\sim$ 1 meter which ensured both complete conversion of O_3 to Cl and the thermalization of ClO. The decrease in OH signal due to reaction with ClO was then measured. Following this measurement, the ClO concentration was changed by altering the O_3 concentration, and the OH signal was remeasured. Typically five O_3 concentrations (i.e. ClO concentrations) were employed. Finally, the OH source was turned off to remeasure background. Following these measurements, the injector was moved to a different position and the whole experiment repeated. Usually, five injector positions (i.e., reaction times) were employed to span at least 2 1/e times. During all measurements, care was taken to ensure maintenance of constant pressure and constant flow velocity. The flow velocity was in the range $\sim$1300 - 1700 cm sec^{-1} in all experiments.

Results and Discussion

As mentioned earlier, all kinetics experiments were carried out under pseudo-first order conditions with [ClO] in excess over [OH]. Therefore, [OH] should follow simple first order kinetics, i.e.,

$$[OH]_t = [OH]_o \, e^{- k_1[ClO]t} \qquad (I)$$

where $t = d/\bar{v}$, d is the distance from the tip of the injector to the detector, $\bar{v}$ is the linear gas flow velocity in the tube, and $[OH]_o$ is the concentration of OH in the absence of ClO (and the presence of Cl_2). Equation I can be rearranged to yield,

$$\ln \frac{[OH]_o}{[OH]} = k_o[ClO]\, d/\bar{v} \quad . \qquad (II)$$

Figure 2 shows a plot of $\ln [OH]_o/[OH]$ vs [ClO] at a fixed value of d and $\bar{v}$; the plot is linear. $\bar{v}$ was calculated from the net mass flow of gases through the tube, the pressure in the tube, and the area of cross-section of the tube. Since [ClO] was known, k_1 could be calculated from the plot in figure 1. Such measurements were carried out at various values of d. Alternatively, at a fixed concentration of ClO, the concentration of detected OH at various reaction times, i.e., at various values of d at a fixed v, were measured. One such plot is shown in Figure 3. The slope of the line gives the pseudo-first order rate constant $k' = k_1[ClO]$. Values of k' at various values of [ClO] were measured and then k' vs [ClO]plots (such as the one shown in Figure 4 were generated. k_1 values were obtained from the slopes of these plots. In the absence of ClO , k' should be zero. However, we measured a negative value $\sim -2\ s^{-1}$. This is interpreted to represent the increased wall loss as the injector was thrust farther into the flow tube. It was found that the value of k_1 obtained by this method agreed well with that calculated at fixed values of d. However, since the wall loss on the injector could be varying to some degree, we preferred using the method of fixed d. All the values reported here were calculated by this method.

Cl atom concentration was much greater than that of ClO, it is possible to obtain an analytical solution for the temporal behavior of OH in this system (i.e., reaction (1), followed by reactions 7a and 7b):

$$[OH] = \frac{[OH]_o}{(\alpha^2 - 4\beta)^{\frac{1}{2}}} \{(k_7[Cl] + \lambda_1)e^{\lambda 1 t} - (k_7[Cl] + \lambda_2)\, e^{\lambda 2 t}\} \qquad III$$

where

$$\alpha = k_1[ClO] + k_7[Cl]$$

$$\beta = (k_7[Cl]) \times [(k_1[ClO]) - (k_{1a}[ClO]) \times (k_{7b}[Cl])$$

$$\lambda_1 = \frac{-\alpha + (\alpha^2 - 4\beta)^{\frac{1}{2}}}{2}$$

and $$\lambda_2 = \frac{-\alpha - (\alpha^2 - 4\beta)^{\frac{1}{2}}}{2}.$$

The measured value of [OH] actually followed Equation III while we assumed Equation I to be valid. Therefore, the measured value of $[OH]_0/[OH]$ can be corrected by using the values of k_{7a} and k_{7b} obtained by Lee and Howard:[7]

$$k_{7a} = (1.8 \pm 0.5) \times 10^{-11} \exp[(170 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \qquad IV$$

and

$$k_{7b} = (4.1 \pm 0.8) \times 10^{-11} \exp[-(450 \pm 60)/T) \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1} \qquad V$$

To a first approximation, by assuming that reaction (7) is very rapid compared to reaction (1), it can be shown that,

$$k_1(\text{corrected}) = k_1(\text{measured}) \times [1 - \{\frac{k_{7b}}{k_7} \times (1 - \frac{k_{1b}}{k_1})\}]^{-1} \qquad \text{VI}$$

where $k_7 = k_{7a} + k_{7b}$ and $k_1 = k_{1a} + k_{1b}$. However, we employed a rigorous iterative procedure where each value of measured $[OH]_o/[OH]$ (at various values of d and [ClO]) was corrected by using Equations III and I. These corrections were made by assuming that k_{1b} is zero. The justification for this assumption is twofold: for reaction (1) to have a significant (i.e. > 10%) branching ratio to yield HCl is not very likely since the reaction has to proceed via a four-centered complex and (b) if $k_b \neq 0$, then it is very easy to correct our data accordingly. (For example using Equation VI). It was found that the difference between using Equation VI vs the iterative procedure is minimal. As expected, the concentration of Cl atoms had no effect as long as it was much greater than that of ClO. In Figures 2, 3 and 4, the corrected points are shown as separate lines. The bimolecular rate coefficient obtained using the corrected data is also tabulated in Table I. The corrections for individual data points ranged from $\sim$ 5% to $\sim$ 30%, while the value of k_1 changed by $\sim$ 13% at 248 K and $\sim$ 30% at 335 K. The larger corrections at higher temperatures is due to the increasing values of k_{7b}/k_7 with temperature. As seen from Table I, the corrected data show a negligible temperature dependence and indicate that the temperature dependence seen in the uncorrected data is due to the variation of k_{7b}/k_7 with temperature. A fit of the corrected data to an Arrhenius expression yields:

k_1 was measured at five temperatures ranging from 248 to 335 K. The obtained values, along with the overall error limits (95% confidence limit including random errors and estimates of systematic errors), are shown in Table I. The usual testing for the presence of complicating secondary reactions-variations of $[OH]_o$, $\bar{v}$, $[Cl]_o$, and pressure (1.0 to 4 Torr) were carried out and found to have no effect on the measured value of k_1. Since the absolute concentrations of OH and ClO were accurately known and the concentration of Chlorine atoms was very much larger than that of ClO, it was easy to show (when we carried out the measurements in 1981) that no secondary reactions were affecting our measurements. In addition, HO_2, the reaction product was expected to be quickly converted to non-reactive HCl via the reaction,[3,4,5,6]

$$Cl + HO_2 \rightarrow HCl + O_2 \ . \qquad (7)$$

In fact, the choice of this particular chemical system was due to its simplicity and the fact that ClO concentration need not be directly measured. However, it has been recently discovered[7] that reaction (7) has multiple product channels, i.e.

$$Cl + HO_2 \rightarrow HCl + O_2 \qquad (7a)$$

$$\rightarrow OH + ClO. \qquad (7b)$$

The effect of reaction (7b) on our experiments is the regeneration of OH, thereby leading to an erroneously low value of k_1. However, since the

$$k_1 = (9.2 \pm 6.5) \times 10^{-12} \exp[(66 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}.$$

We prefer to quote an unweighted average temperature independent value of $(11.7 \pm 3.3) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1} for k_1 over the range 248°-335°K. The quoted errors completely bracket the range of errors shown in Table I.

A short justification of the chemical system that was chosen to study this reaction is in order. First, in the absence of a direct method for ClO monitoring in our laboratory, it is prudent to use the Cl + O_3 reaction to produce ClO since its concentration could be accurately calculated. Second, the presence of excess Cl atoms was needed not only for complete conversion of O_3 to ClO but also to ensure that ClO was not depleted in the flow tube via reactions such as ClO + ClO → ClOO + Cl, since Cl atoms would regenerate ClO.[8,9] Third, it seemed most appropriate to convert the very reactive product of reaction 1, HO_2, into a stable species.

A comparison of our uncorrected value of k_1, $(9.3 \pm 2.0) \times 10^{-12}$ cm^3 molecule^{-1}s^{-1} with that of Leu and Lin[1], $(9.1 \pm 1.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} shows excellent agreement. Leu and Lin[1] did not correct their values of k_1 to take into account the effect of reaction 7b since, at the time of their measurement, it was generally believed that the Cl + H_2O reaction yielded only HCl + O_2. Like the present investigation, Leu and Lin used excess Cl atoms in their kinetics experiments and the above described correction procedure is applicable to their measurements also. Therefore, it is clear that the agreement between the two studies is good.

Using the currently recommended value of 5.0×10^{-12} cm^3 molecule^{-1}s^{-1} for the rate coefficient for the reaction

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (8)$$

and the branching ratio data obtained by Leu and Lin,[1] we recalculated k_{1a}/k to be greater than 60% at 298°K. Reaction (1b) which requires a four-centered reaction mechanism is unlikely to be competitive with the fast reaction rate measured for the overall process and therefore k_{1b}/k_1 is likely to be much less than 40%. However, a definitive determination of k_{1b}/k_1 is still needed for stratospheric modeling purposes.

Assuming $k_{1b} = 0$, we can use our measured value of k_1 in conjunction with the value of k_{7b} determibed by Lee and Howard[7] to calculate the equilibrium constant, K, at 298 K to be 0.76 for the reaction

$$CL + HO_2 \rightarrow OH + ClO.$$

This equilibrium constant yields a value of 3.1 kcal/mole for $\Delta H^o_{f298°K}$ (HO_2), which is lower than 3.3 kcal/mole obtained using the uncorrected value of Leu and Lin. 3.1 kcal/mole is in better agreement with that calculated by Benson and Shum[10] (3.0 kcal/mole), and overlaps with the upper limit measurement of Howard[11] (2.5 $\pm$ 0.6 kcal/mole).

Reaction (1) can have the maximum impact on stratospheric chemistry at an altitude where the product of [ClO] and [OH] is the maximum, i.e. $\sim$ 40 km. Even at this altitude, Reaction (1) can contribute at most $\sim$ 3% towards converting OH to HO_2 while the majority of the conversion proceeds through the $OH + O_3 \rightarrow HO_2 + O_2$ reaction. Hence, only if k_{1b}/k_1 is significant can Reaction (1) have a large impact on stratospheric chemistry.

Acknowledgments

We thank C.J. Howard for making available data on the Cl + HO_2 reaction prior to publication. This work was supported by the Chemical Manufacturer's Association Technical Panel on Fluorocarbon Research.

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Table I. Rate Coefficients for the Reaction of OH with ClO as a Function of Temperature. The Corrected Values in the Last Column Were Obtained as Described in the Text.

Temperature, K	Uncorrected for Reaction 7 $k \times 10^{12} cm^3 molec^{-1} s^{-1}$ [a]	Corrected for Reaction 7 $k \times 10^{12} cm^3 molec^{-1} s^{-1}$ [a]
248	10.9 ± 2.5	12.3 ± 2.6
257	10.6 ± 2.0	12.7 ± 2.3
260	8.7 ± 1.6	10.5 ± 2.1
298	9.3 ± 2.0	12.0 ± 2.5
335	8.6 ± 1.2	11.0 ± 2.0
		11.7 ± 3.3

a) Overall estimated error which includes 2σ statistical error.

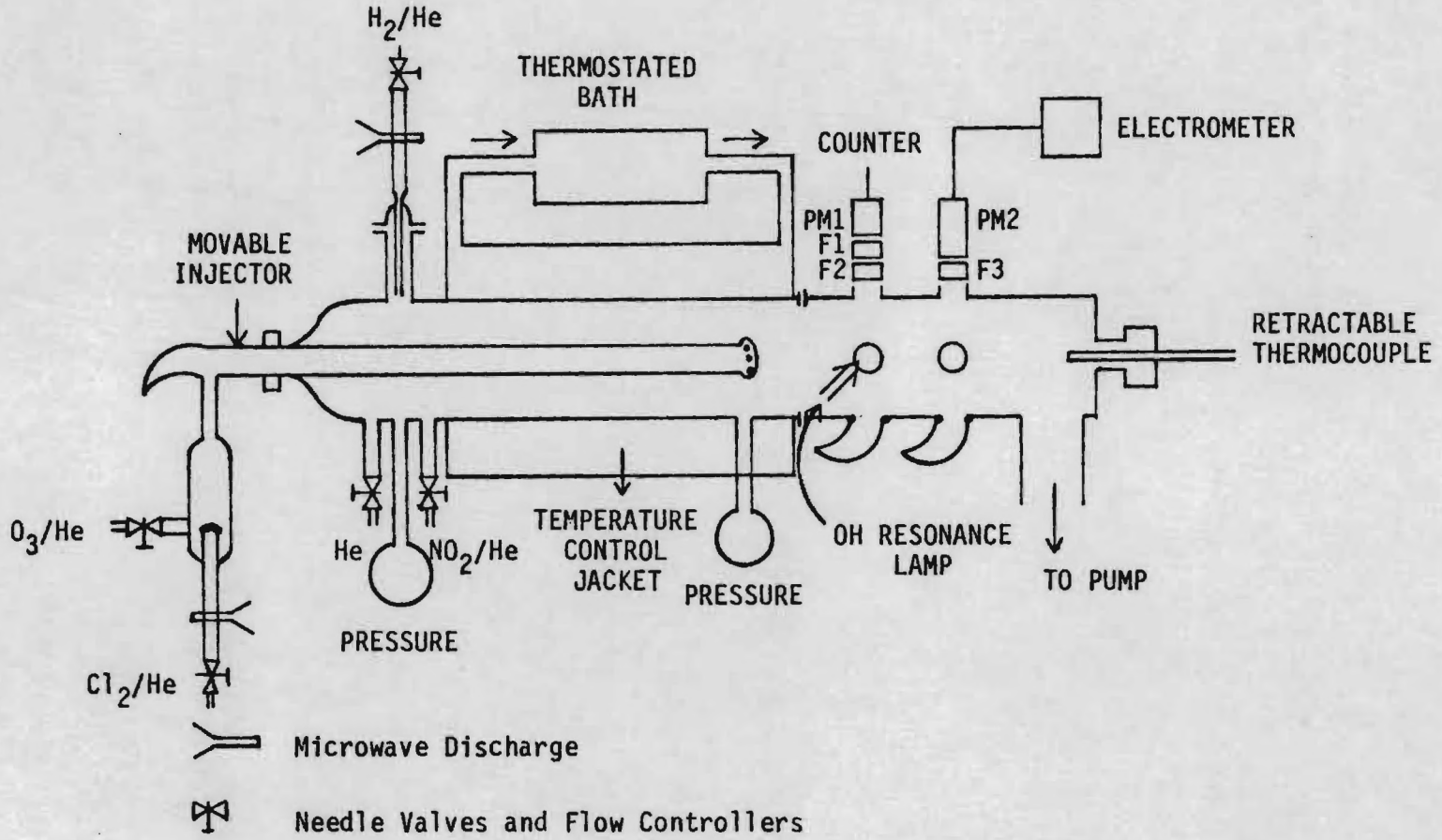

Figure 1. Schematic diagram of the discharge flow - OH resonance fluorescence apparatus. PM1, F_1, and F_2 combination was used for OH detection. PM2 and F_3 combination was used for Cl atom detection.

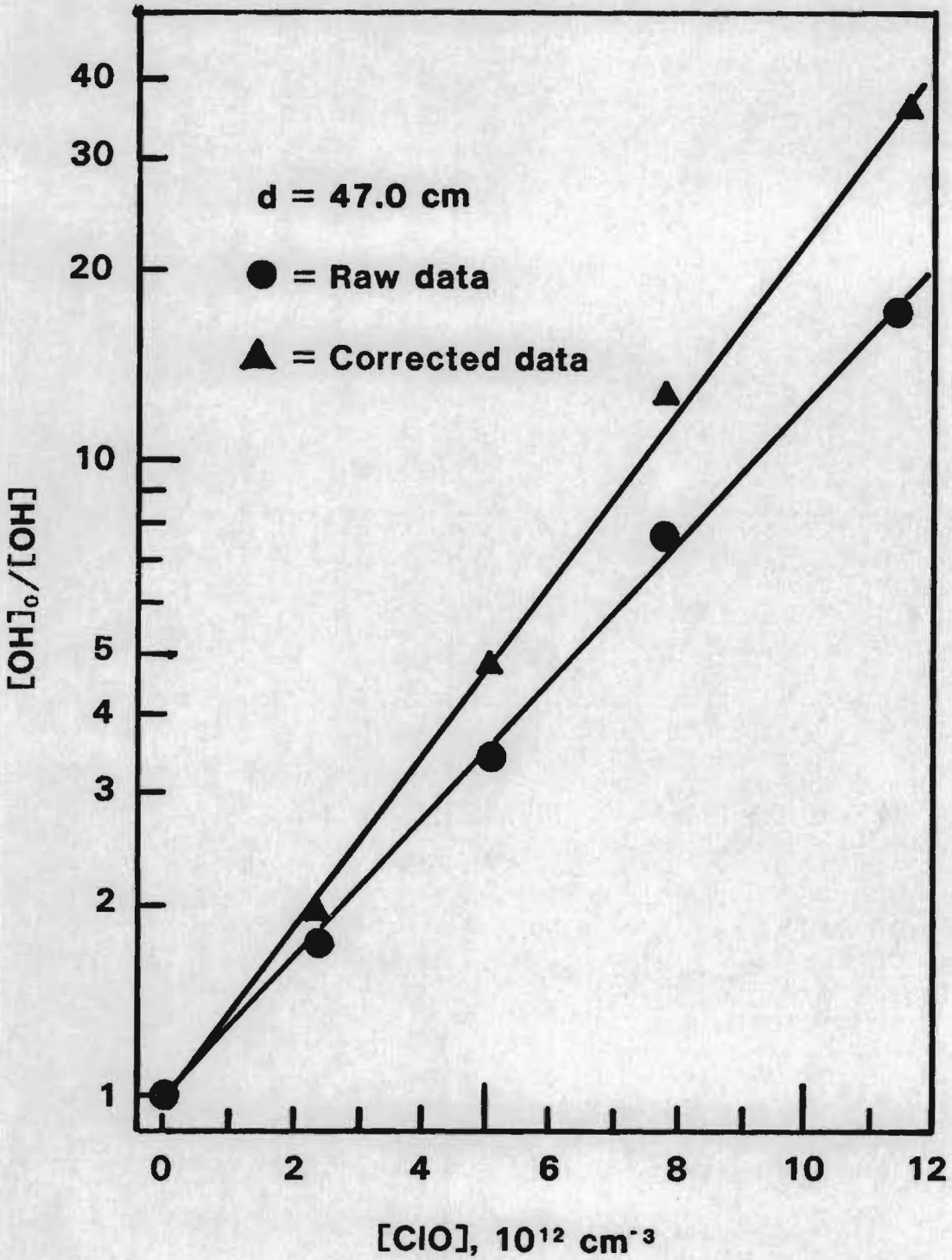

Figure 2. Plot of In $[OH]_0/[OH]$ vs [ClO] at one value of d. The filled circles are the measured values. The filled triangles were obtained by correcting the measured data using the procedure described in the text for the interference due to reaction (7).

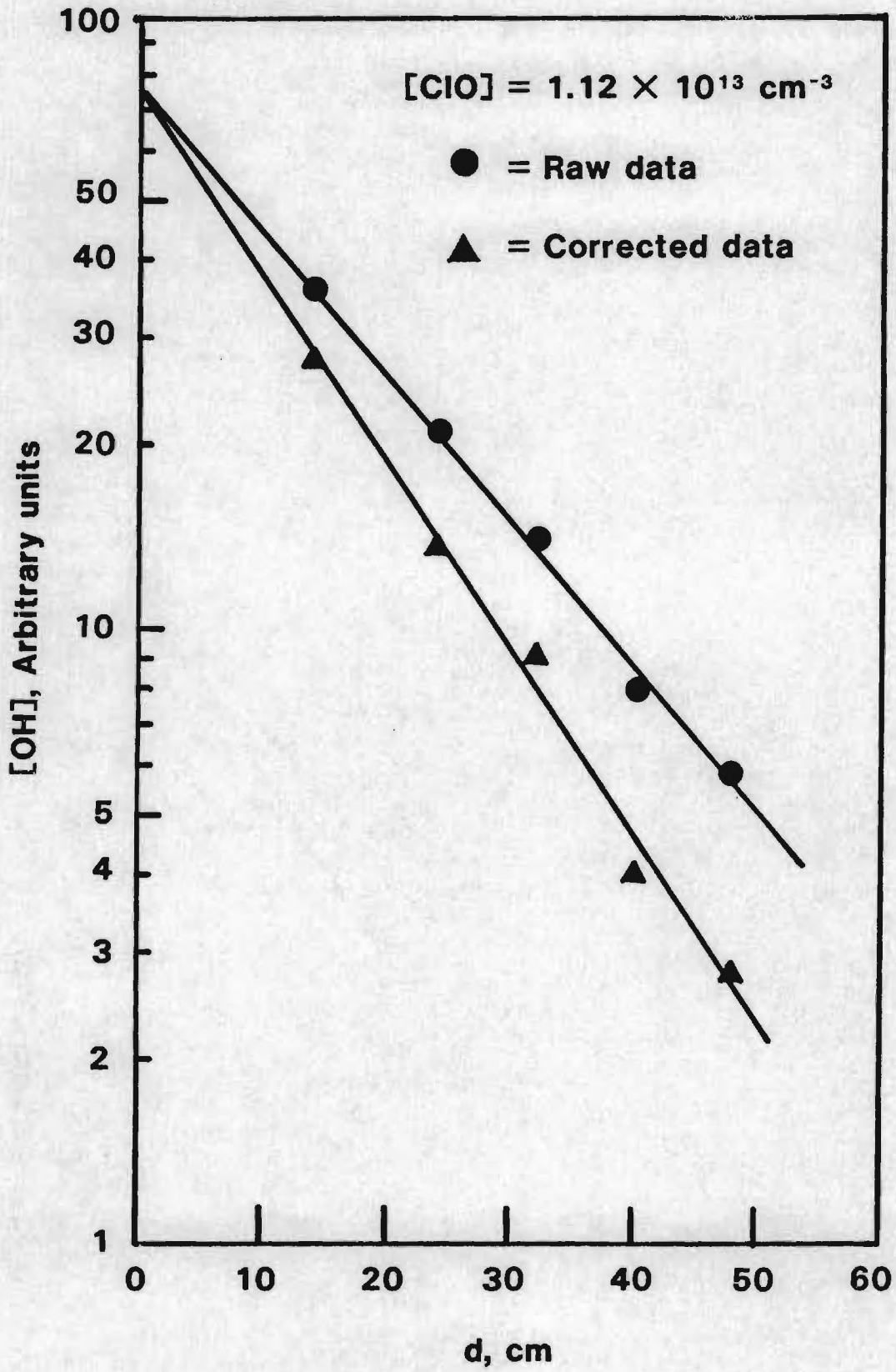

Figure 3. Plot of In [OH] vs d at one value of [ClO]. The filled circles are measured values. The filled triangles were obtained by correcting the measured data using the procedure described in the text for the interference due to reaction (7). The slope of the plots yield k′ values.

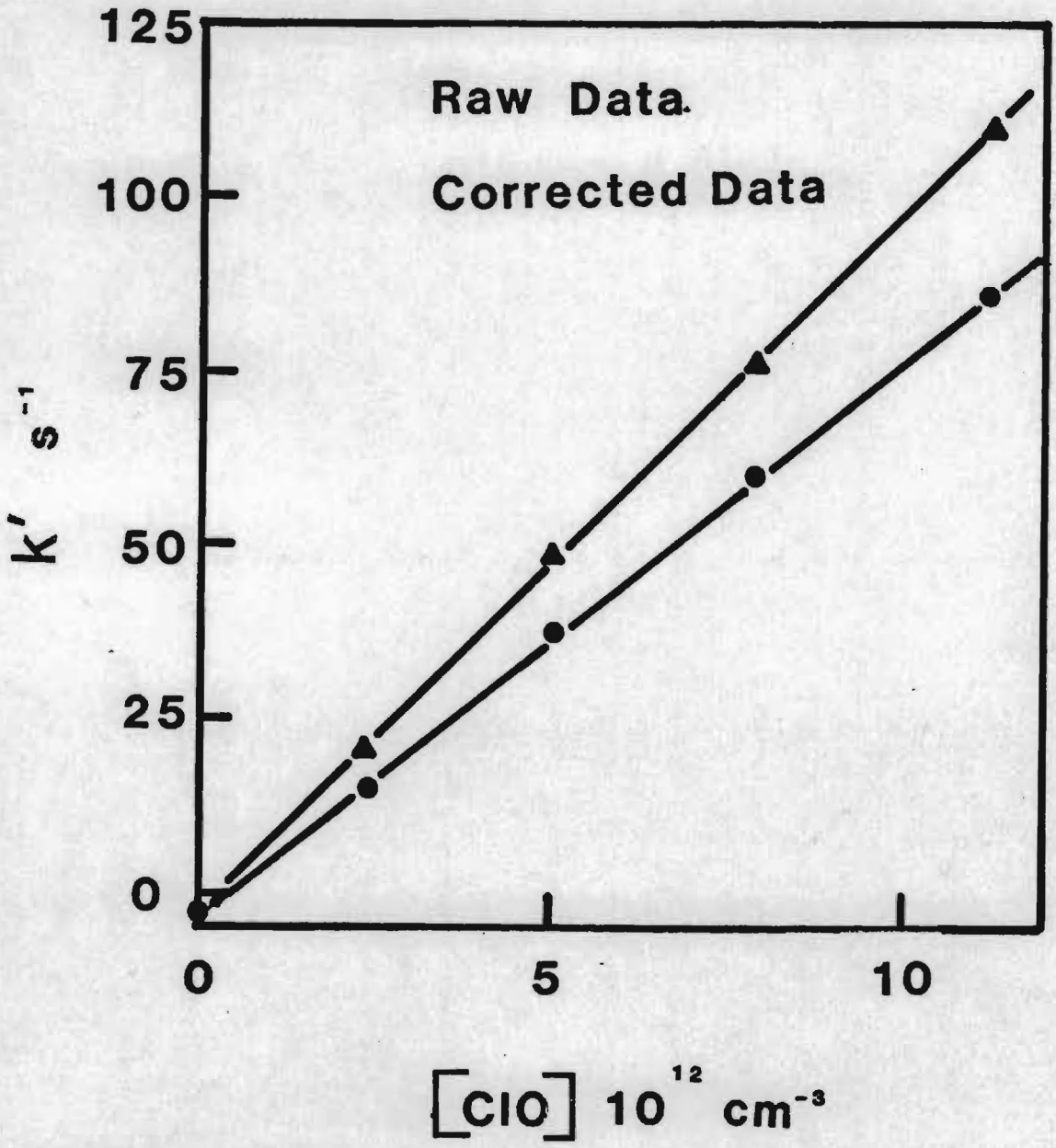

Figure 4. Plot of k′ vs [ClO]. k′ values were obtained from plots such as those in Figure 3. The filled circles and triangles have the same meaning as in Figures 2 and 3. The slope of the plots yields k_1 values.

Chapter II

SUBMILLIMETER DETERMINATION OF HCl CONCENTRATIONS IN DISCHARGE FLOW EXPERIMENTS

By

J. J. Gallagher

V. Brady

Submillimeter Wave Determination of HCl Concentrations in Discharge Flow Experiments

1. Introduction

The millimeter-submillimeter wavelength region provides several opportunities for the investigation of molecular spectra. This region for spectroscopic purposes can be defined as the region from 3 mm to 50 μm. Within this spectral region, the molecular transitions are mainly rotational. With the availability of coherent sources, the resolution of spectra can be very high. Coherent sources include optically pumped lasers, klystrons, carcinotrons (BWO's) and solid state sources (Gunn oscillators and IMPATTS). With the exception of optically pumped lasers and carcinotrons, the coherent sources oscillate at frequencies less than 220 GHz (λ = 1.36 mm). Higher frequencies are achieved with the low frequency sources by harmonic generation or by nonlinear mixing of the output of the low frequency source with the output of a laser or carcinotron. The optically pumped lasers are fixed frequency devices and are limited to use in either cases of coincidence with molecular transitions or cases in which Zeeman or Stark tuning can be employed to bring the molecular transition into coincidence with the laser transition.

The tunable sources can not only be adjusted in frequency to coincide with a molecular transition frequency, but they can be frequency swept through a resonance or can be phase-locked to a precise frequency. The phase-locking scheme is appropriate to high sensitivity spectroscopy since it allows a step-tuning by variation of the originating source and signal averaging at each step.

The phase-lock technique also provides the means for accurate frequency measurement, since frequency can be read directly at the originating source frequency. The millimeter/submillimeter wave source frequency will have the stability, under most cases, of the originating source. Frequency standards and frequency synthesizers which are commercially available and can serve as the originating source in a phase-locking chain have short-term stabilities of 1 part in 10^{10}-10^{11}. These techniques will be discussed later with respect to the molecular flow experiments.

In addition to the advantages of coherent sources in the millimeter-submillimeter spectral region, the region is characterized by its use of quasi-optical techniques. Because of the reduction in size in waveguide components as wavelength is reduced, propagation losses become quite large. In order to avoid these losses, oversize structures employing a combination of waveguide (usually used for the purpose of launching a free - space wave) and optical techniques are used. Whereas the use of quasi-optical techniques is often a necessity, it also has many advantages since one can combine the best of waveguide and optical techniques. This is particularly the case for spectroscopic applications since one can provide oversize multi-pass structures, the walls or mirrors of which interact relatively little with the molecular species under investigation. This results in an advantage for flowing systems and for transient molecules. Actually, non-flowing short-lived molecular species have been observable for relatively long periods of time in glass or quartz cells whereas they are usually not observable in metal waveguide cells. The non-metallic cells are fed by horn and lens combinations.

A quasi-optical device which has been used for several spectroscopic applications is the Fabry-Perot interferometer. This device, in the long wavelength region, can be flatplate, fed by horns and lenses or a semi-confocal device fed by waveguide. Some brief comments on the resonator structures will be given in Section 3 with a description of the device which has been built for the discharge flow experiments.

In the sections which follow, we will briefly discuss the millimeter/submillimeter HCl and DCl transitions of interest, comment on the resonant structures which are appropriate for the flow experiments and discuss the relations for determining molecular concentrations, the reactions of interest, molecular concentrations which will be detectable and the experimental work which has been performed thus far.

2. HCl and DCl Rotational Transitions

The hydrogen chloride molecule has its first rotational transition J=0→1 in the region of 625 GHz (λ = 0.48 mm). With 30 GHz = 1 cm^{-1}, this corresponds to a frequency of 20.83 cm^{-1}. Thus, a rotational transition will occur approximately every 20.83 cm^{-1}. This lowest transition is the most accessible for tunable coherent spectroscopy.

The observable rotational transitions for HCl are for the two isotopic species $H^{35}Cl$ and $H^{37}Cl$. The isotopic percentages of chlorine are

Cl^{35}	75.4%
Cl^{37}	24.6%

Each rotational transition for each isotope is split into three hyperfine components by the chlorine nuclear quadrupole moment interaction. The nuclear spin for both ^{3}Cl and ^{37}Cl is 3/2. The J=0→1 (V=0 ground vibrational state) rotational transition center frequencies are:

$H^{37}Cl$: ν_o = 624,915 MHz

and

$H^{35}Cl$: ν_o = 625,866 MHz

with the following hyperfine splittings: J=0→1, v=0

	F→F'			
$H^{35}Cl$:	3/2	3/2	625.854	(16.7%)
	5/2	3/2	625.864	(50%)
	1/2	3/2	625.876	(33.3%)
$H^{37}Cl$:	3/2	3/2	624.905	(16.7%)
	5/2	3/2	624.913	(50%)
	1/2	3/2	624.923	(33.3%)

These frequencies are the experimental values reported by DeLucia et al. [1]. Two important HCl parameters which are required for calculation of molecular concentrations in flow experiments are the dipole moment and linewidth parameter. Experimental values derived directly from submillimeter transitions do not exist but are inferred from Townes and Schawlow [2] to give the electric dipole moment for HCl of 1.18 debye.

A more easily attainable frequency for tunable millimeter wave coherent sources occurs for the deuterated species, DCl. The rotational transition, $J=0\rightarrow 1$, $v=0$ for this molecule occurs at the following frequencies [3]:

		$F\rightarrow F'$		
$D^{37}Cl$	$J=0\rightarrow 1$,	3/2	3/2	322, 339.09 MHz
	$v=0$	5/2	3/2	322, 352.33
		1/2	3/2	322, 362.94
$D^{35}Cl$	$J=0\rightarrow 1$,	3/2	3/2	323, 282.28 MHz
	$v=0$	5/2	3/2	323, 299.17
		1/2	3/2	323, 312.52

Since the DCl transition frequency is practically half of the HCl frequency, it is more accessible to harmonic generation from lower frequency sources. In the light of problems encountered in obtaining sufficient power at 625 GHz in the experimental phase of this program, it might be advisable to perform initial experiments at 323 GHz. This will be discussed in later sections.

3. Fabry-Perot Interferometer Techniques

The Fabry-Perot interferometer is a conventional optical instrument, but it has become a useful millimeter wave device only in recent years. It has been used to serve as band-pass filters, receiver duplexers and resonators for spectroscopic investigations. As a tool for spectroscopy, the Fabry-Perot devices have been employed as a flat plate, a semi-confocal or a confocal interferometer. They can be fed by horn/lens combinations or by waveguide. One might argue that these open structure devices are not truly interferometers but they do serve as excellent cells for millimeter and submillimeter wave investigations. In addition to being an open structure/large volume cell, it provides an equivalent long absorption path. For experiments such as that of interest to this program, a very large interferometer which would have a large effective absorption path would not be suitable. The molecular flow would not fill the cell so that it would not be possible to utilize the whole path length nor even estimate accurately the equivalent path for the gas. Thus, it will be necessary to use a smaller resonator which will be approximately filled by the flowing gas. Although the effective absorption pathlength is reduced, the "fill factor" of the gas will be approximately unity.

The interferometer to be employed is shown in Figure 1. It is housed in a 2" diameter glass pipe which is adapted to the end of the fluorescence flow system. The resonator is fed by two waveguides in the flat plate of a semi-confocal interferometer. Since the resonator must operate at several wavelengths, it is not always a semiconfocal interferometer. Figure 2 shows the configuration of a semiconfocal interferometer or an approximate one. The radius of curvature of the interferometer is b and the separation of plates is d, so that the condition of resonance is

$$\frac{4d}{\lambda} = 2q + (1 + m + n)\left(1 - \frac{4}{\pi} \tan^{-1} \frac{b-d}{b+d}\right).$$

For d = b, the system is confocal and

$$\frac{4b}{\lambda} = 2q + (1 + m + n)$$

where q, m and n are integer. For the flat plate at R/2, the semi-confocal interferometer results. Because of boundary conditions imposed on the electric field by flat mirrors, index q is restricted to "even" integral values. The index q refers to the number of half wavelengths in a confocal system. The factor $4b/\lambda$ must take an integral value , whereas, for a nonconfocal system, $4d/\lambda$ as an integral value is not imposed as a condition for resonance. Modes associated with a confocal system are degenerate in (m + n). Degeneracy is removed in the non-confocal case.

An interferometer parameter of importance is the Fresnel number

$$N = \frac{a^2}{b\lambda}$$

(in the form appropriate for a confocal or semiconfocal interferometer). This parameter gives the diffractive losses for the interferometer for each transverse mode. Figures 3 and 4 (from Reference 4) shows the diffraction loss per transit (in dB) for the TEM_{00} and TEM_{01} mode of a stable resonator with circular mirrors. For the confocal (or semiconfocal) case, $|g| = 0$, the losses for $N < 1$ are greater for the TEM_{01} mode than for the TEM_{00} so that the TEM_{01} mode will not be excited for small N-values whereas the TEM_{00} will be excited but with losses given by Figure 3 for the particular N. The resonator of Figure 1 has $N \simeq 0.2$ for $\lambda = 0.48$ mm corresponding to losses of ~4 dB for TEM_{00} and ~20 dB for TEM_{01}. The 4 dB loss may be large for the TEM_{00} mode resulting in loss of Q but testing will determine if this is the case. If the Q has to be increased, we can cut a curved plate of small radius of curvature after the initial tests. Thus, for b = 1.4 inches, N = 0.6 so Power Loss for TEM_{00} = 0.1 dB and for TEM_{01} = 1 dB.

The interferometer plates of the resonator of Figure 1 are goldplated. Figure 5 shows some of the dimensions of the apparatus. The curved plate is mounted and spring loaded for tuning to frequency. The alignment of the plates, which requires minimal adjustment for the operating wavelengths, is achieved by adjustment of the mounting flanges on the o-rings. The coupling holes of the flat plates are small and can be enlarged if increased coupling is necessary. For best Q-values, usually small coupling holes are optimum.

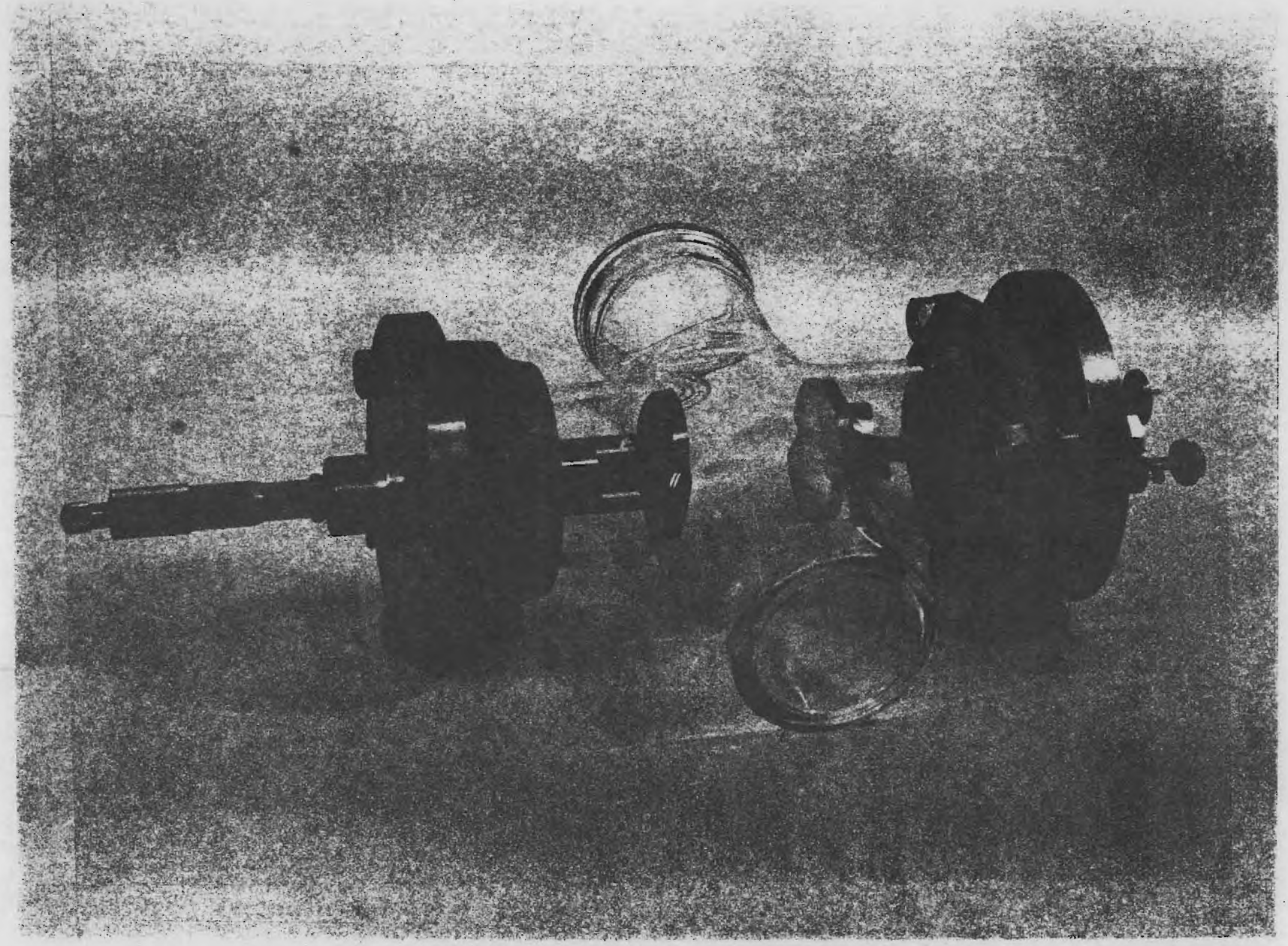

Figure 1. Semiconfocal Fabry-Perot Resonator for 625 GHz observation of $H^{35}Cl$ Rotational Transition.

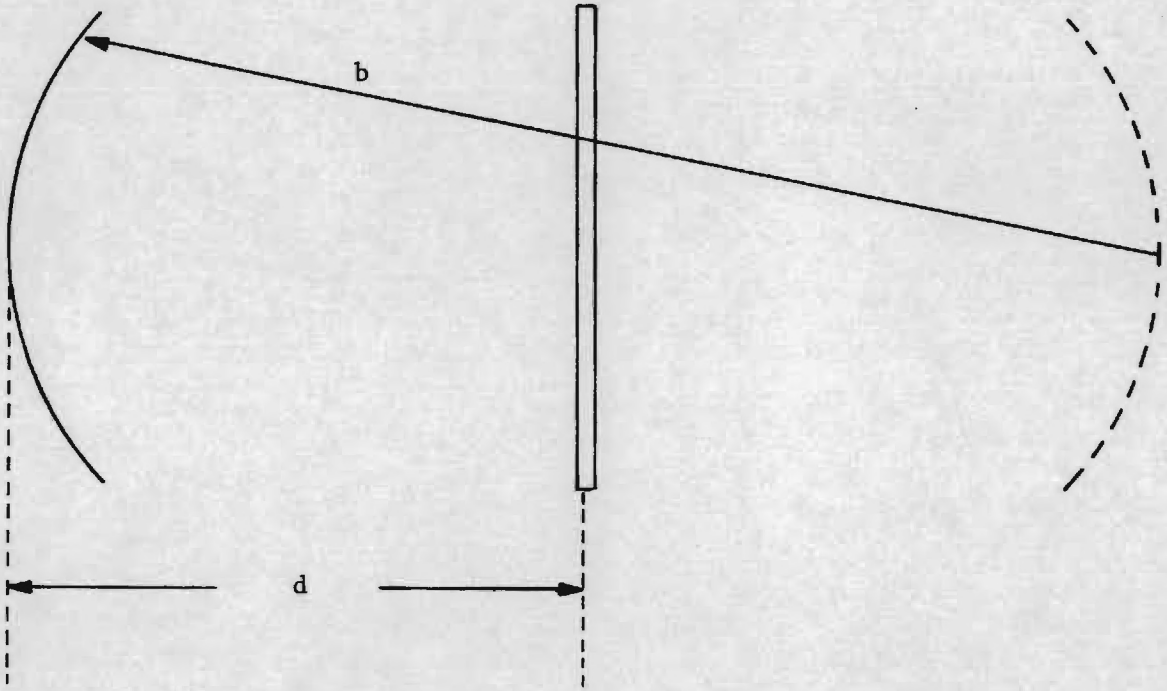

Figure 2. Semiconfocal Resonator Configuration.

b = radius of curvature of curved plate
d = plate separation

where q, m and n are integer. For the flat plate at R/2, the semi-confocal interferometer results. Because of boundary conditions imposed on the electric field by flat mirrors, index q is restricted to "even" integral values. The index q refers to the number of half wavelengths in a confocal system. The factor $4b/\lambda$ must take an integral value , whereas, for a nonconfocal system, $4d/\lambda$ as an integral value is not imposed as a condition for resonance. Modes associated with a confocal system are degenerate in (m + n). Degeneracy is removed in the non-confocal case.

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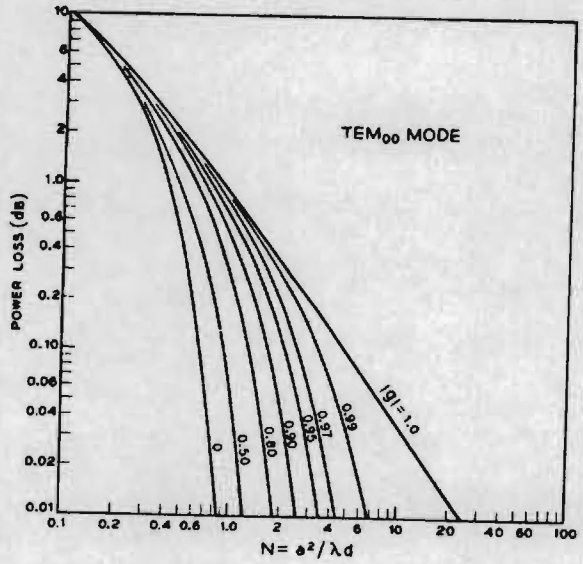


Figure 3. Diffraction loss per transit (in decibels) for the TEM_{00} mode of a stable resonator with circular mirrors.

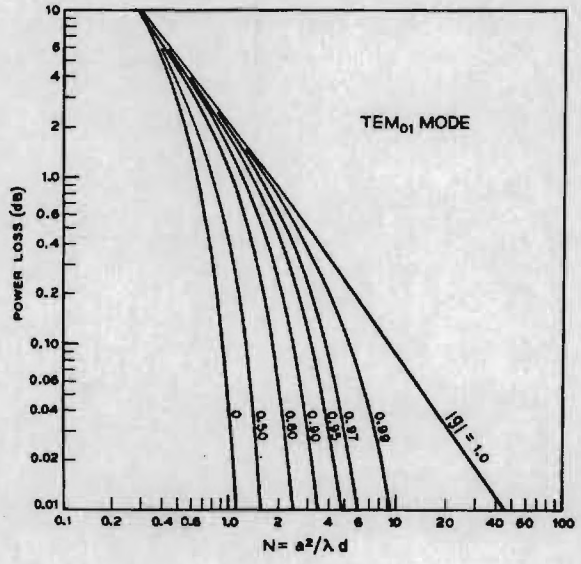


Figure 4. Diffraction loss per transit (in decibels) for the TEM_{01} mode of a stable resonator with circular mirrors.

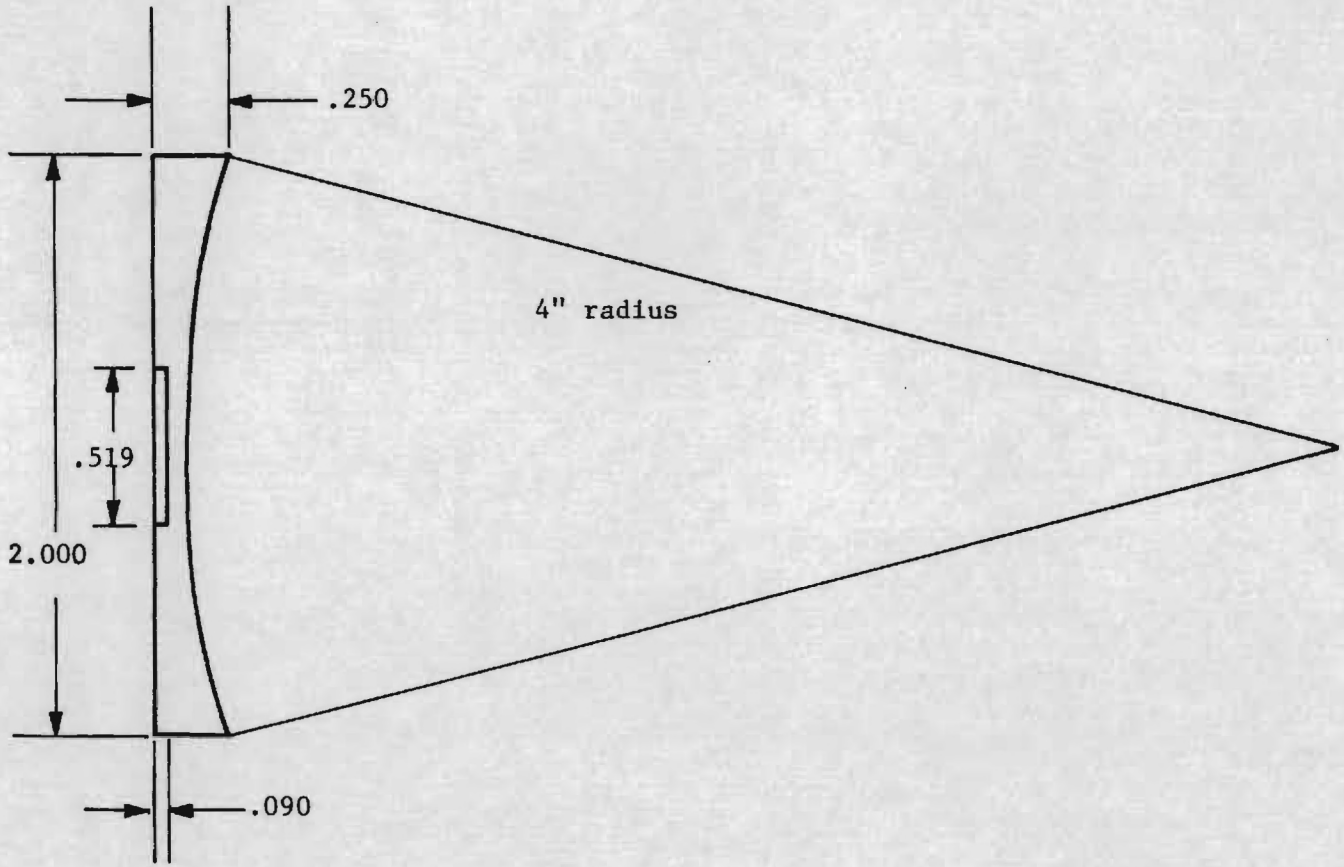


Figure 5a. Dimension of the Fabry-Perot Interferometer plates.

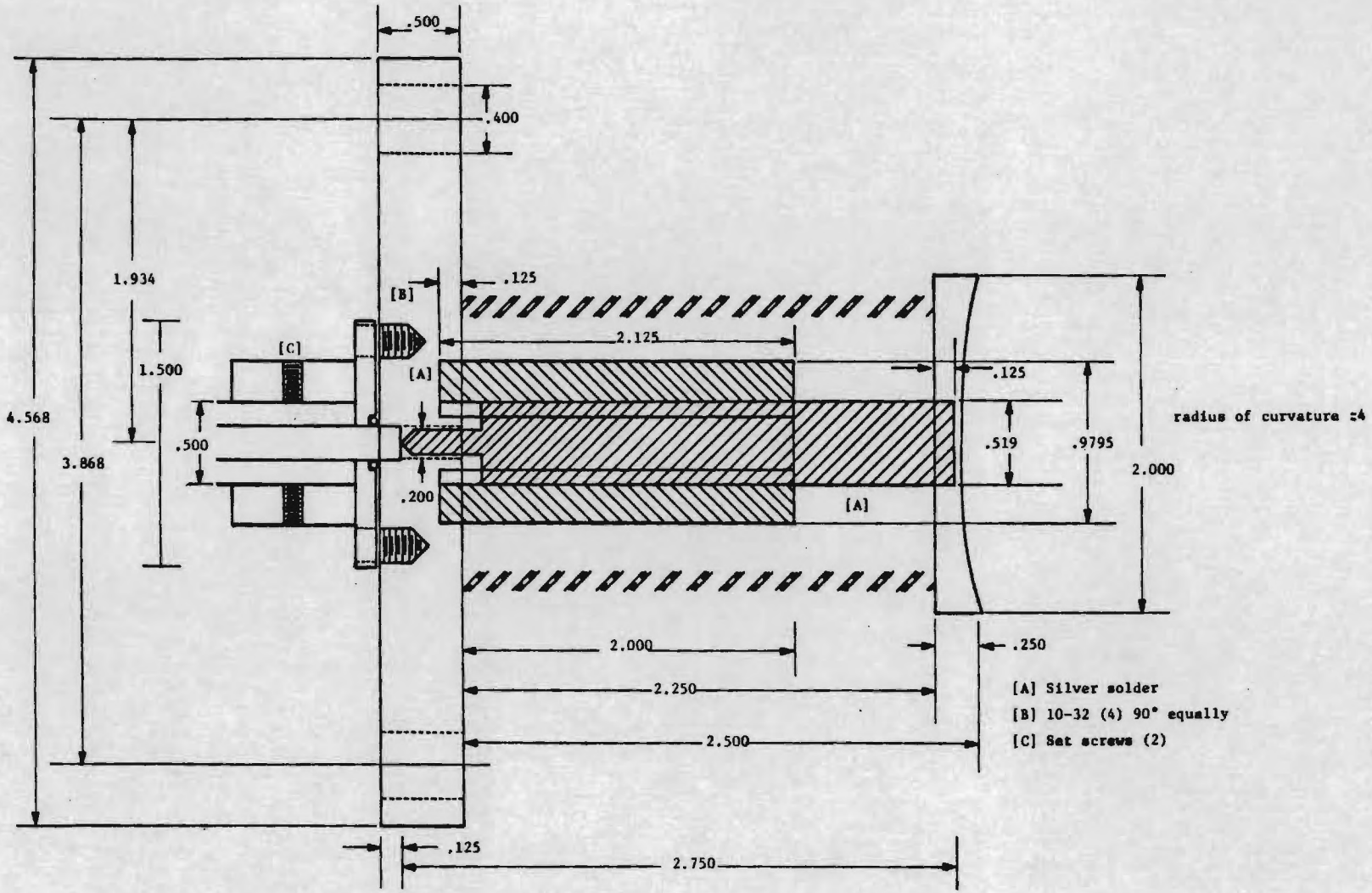


Figure 5b. Mounting of Curved Interferometer Plate on Chamber Plate.

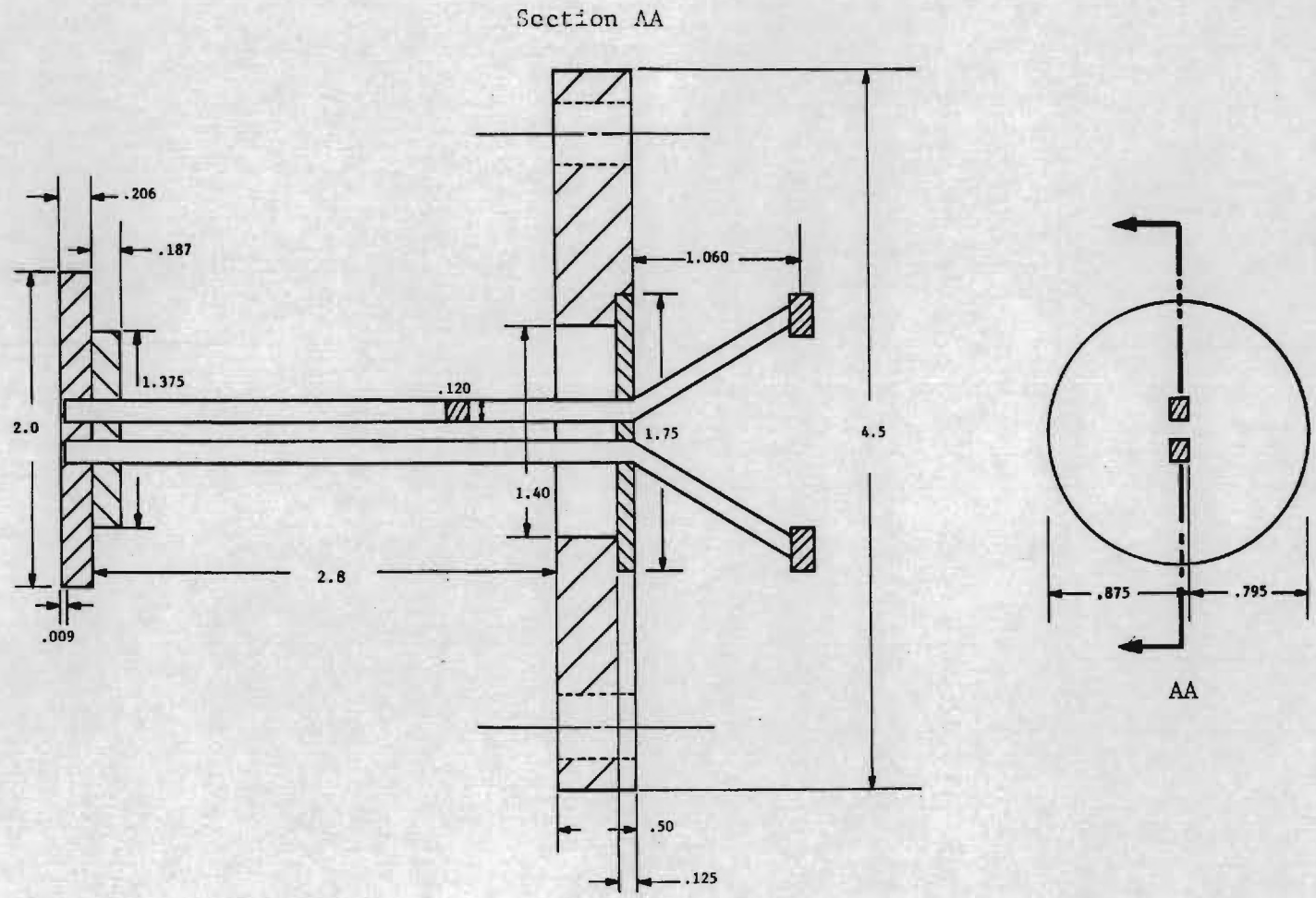


Figure 5c. Waveguide coupling to Flat Plate of Interferometer.

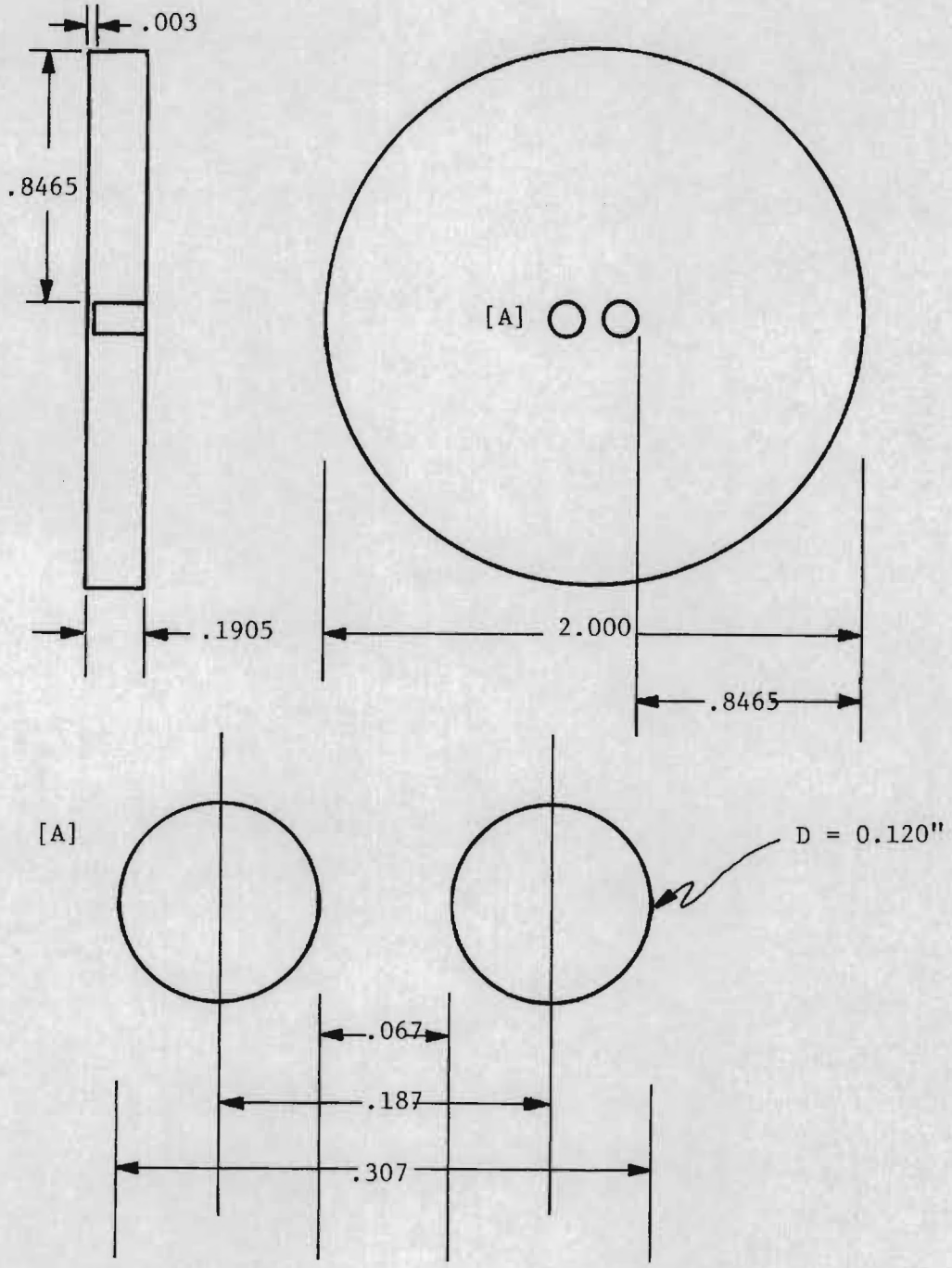


Figure 5d. Dimensions of waveguide coupling holes to Interferometer Flat Plate.

Of the two waveguides, one is attached to the harmonic generator providing the input signal and the other is the output to the receiver mixer or detector.

To determine the absorption coefficient of a vapor filling the interferometer volume, the Q of the interferometer is measured with (Q_1) and without (Q_0) the absorbing gas, and the resulting equation for gas loss is

$$\gamma = \frac{2\pi}{\lambda}\left(\frac{1}{Q_1} - \frac{1}{Q_0}\right) = \frac{2\pi}{\lambda} \tan \delta \ \text{cm}^{-1}$$

If A is the output of a loosely coupled square low detector at the output of the Fabry-Perot resonator, then

$$\frac{Q_0}{Q_1} = \left(\frac{A_0}{A_1}\right)^{\frac{1}{2}}$$

and

$$\gamma = \frac{2}{Q_0}\left[\left(\frac{A_0}{A_1}\right)^{\frac{1}{2}} - 1\right] \text{cm}^{-1}$$

The equivalent path is

$$\text{EPL} = \frac{Q_1 \lambda}{2\pi} \ .$$

The absorption coefficient can be calculated by accurate measurement of the resonance amplitudes with the molecular gas in and out of the resonator. For a semiconfocal interferometer similar to the one to be used in these experiments, we have measured $Q \approx 1000{,}000$ so that an equivalent absorption path length on the order of 7.6 m can be expected.

4. Molecular Concentration Relations

In performing calculations of the concentrations of HCl in flow-discharge experiments, the linewidth for each transition is an important parameter. The Doppler broadening is small for the J=0⟶1 rotational transition of HCl, being ν_D = 0.65 MHz at 625 GHz, and, for a flow system with velocity perpendicular to the Fabry-Perot interferometer axis, will for all purposes be zero.

Some uncertainty exists in the pressure-broadening linewidth parameter, since it has not been measured for the submillimeter rotational transitions. The environment of the flow discharge system is also different from that found in a stationary gas mixture. Collision processes differ considerably as do the constituents other than the molecule being observed. For very low pressures in a flow system, the linewidth is the uncertainty broadening determined by the observation time for the molecules in the resonator. At the pressures encountered in the flow-discharge experiments, it will be assumed that the line-width parameter of the conventional stationary measured line-width value is applicable. For the most accurate value, it is necessary to measure the line-width in the flow system. The techniques for linewidth measurements will be discussed later.

To calculate the molecular concentration of HCl, we can use the Van Vleck-Weisskopf equation for the transition absorption coefficient,

$$\gamma = \frac{8\pi^2 N f |\mu_{ij}|^2 \nu^2 \Delta\nu}{3ckT[(\nu - \nu_0)^2 + (\Delta\nu)^2]}$$

where $f = f_v f_J$ and $f_v = 1$

$$f_J = (2J + 1)\frac{hB}{kT} e^{-kBJ(J+1)/kT}$$

and

$$|\mu_{ij}|^2 = \mu^2 \frac{(J+1)}{2J+1}$$

for the transition $J+1 \longleftarrow J$.

Also,

$h = 6.6256 \times 10^{-27}$ erg sec
$N = \#$ molecules/cm^3
$c = 2.997929 \times 10^{10}$ cm/sec
μ = HCl dipole monent
ν_o= center frequency of the transition
$k = 1.38054 \times 10^{-16}$ erg/degree
$T = 300^oK$
$\Delta\nu$= line-width parameter
B = HCl rotational constant
= 312,991.30

The center frequency for the i^{th} quadrupole HFS transition will then have the peak absorption of

$$\gamma_{oi} = \frac{8\pi^2 NhB(J+1)\mu^2}{3c(kT)^2} \nu_{oi}^2 e^{\frac{-hBJ(J+1)}{kT}}$$

if there is no overlap of the three quadrupole hfs transitions. Otherwise, we must add the contributions at each frequency from the three hfs components for each isotope. In the above relation for γ_{oi}, ν_{oi} indicates the center frequency for each quadrupole transition.

For the case of overlapping lines, the absorption coefficient for the rational transitions for one isotopic molecular species is given by

$$\gamma = \sum_i a_1 a_i \gamma_i$$

where a_1 is the isotopic percentage, a_i is the nuclear quadrupole component percentage of the entire isotope rotational transition. Thus, for $H^{35}Cl$,

$$\gamma = \frac{8\pi^2 NhB\mu^2(J+1)(0.754)}{3(kT)2c} \exp\left[\frac{-hBJ(J+1)}{kT}\right] x\sum_i \left(\frac{a_i \nu^2 \Delta\nu}{(\Delta\nu)^2 + (\nu - \nu_{oi})^2}\right)$$

with the summation over all quadrupole components.

For ν = 625, 864 MHz, the center frequency of the J=0 ⟶ 1, F = 5/2 ⟶ F' = 3/2 component for $H^{35}Cl$, the intensity is

$$\gamma = \frac{8\pi^2(0.754)NhB\mu^2(625,864)^2}{3(kT)^2c} x\left[\frac{0.5}{\Delta\nu} + \frac{0.167\ \Delta\nu}{(\Delta\nu)^2 + (10\ \text{MHz})^2} + \frac{0.333\ \Delta\nu}{(\Delta\nu)^2 + (12\ \text{MHz})^2}\right]$$

The second and third terms within the brackets result from the other quadrupole hfs components. For narrow linewidths, these two terms are negligible. Thus, for a 1 MHz linewidth parameter, $\gamma = 1.828 \times 10^{-16} N\ cm^{-1}$ for 1 Torr, where only the first term in brackets makes a significant contribution to the intensity. For higher pressures,

$$\gamma = 0.914 \times 10^{-16} N\ cm^{-1} \text{ for } P = 2 \text{ Torr}$$

and

$$\gamma = 0.526 \times 10^{-16} N\ cm^{-1} \text{ for } P = 10 \text{ Torr.}$$

Using the line-width parameter estimated from the work of Smith and Giraud [4], one obtains [for $\Delta\nu = p\Delta\nu_1$, and $\Delta\nu_1 = 1.89$ MHz/Torr]

$$\gamma = 0.967 \times 10^{-16} N \text{ cm}^{-1} \text{ for 1 Torr,}$$
$$\gamma = 0.483 \times 10^{-16} N \text{ cm}^{-1} \text{ for 2 Torr}$$
and
$$\gamma = 0.918 \times 10^{-17} N \text{ cm}^{-1} \text{ for 10 Torr}$$

We have also used a linewidth parameter in other work [5] for HCl, i.e.

$$\Delta\nu_1' = 7.37 \text{ MHz/Torr}$$

so that

$$\gamma = 0.248 \times 10^{-16} N \text{ cm}^{-1} \text{ for 1 Torr,}$$
$$\gamma = 0.202 \times 10^{-16} N \text{ cm}^{-1} \text{ for 2 Torr}$$
and
$$\gamma = 0.268 \times 10^{-17} N \text{ cm}^{-1} \text{ for 10 Torr}$$

Summarizing, we then have the following intensities as a function of line-width parameter:

	Intensity (cm^{-1}) x 10^{16}		
	1 Torr	2 Torr	10 Torr
Frequency:			
ν_0 = 625,864 MHZ			
Line width Parameter:			
$\Delta\nu_1$ = 1 MHz/Torr	1.828 N	0.914 N	0.526 N
= 1.89 MHz/Torr	0.967 N	0.483 N	0.0918 N
= 7.37 MHz/Torr	0.248 N	0.202 N	0.0268 N

The importance of linewidth can be seen from this calculation so that an accurate measurement of this parameter is required. The technique of summing over all hfs components for intensity determination is sufficiently accurate for the estimates of this study, but more accurate techniques [6] do exist when the measurements are performed.

5. HCl Detection in Flow Tube

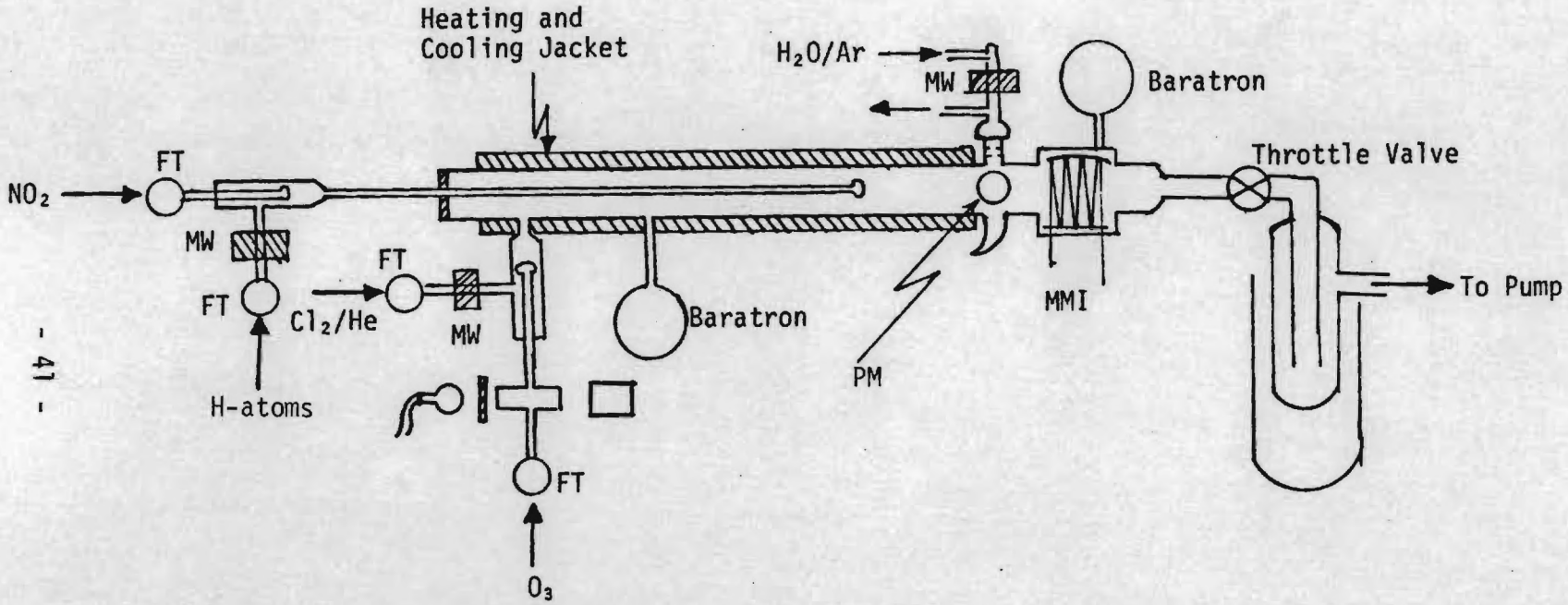
A conventional discharge flow system was coupled to a millimeter wave interferometer detector to measure both k_1 and k_{1a}/k_1. Millimeter wave interferometric techniques have been used to routinely measure small concentrations of species which have high dipole moments. This system is very sensitive and can detect low concentrations of many species.

A schematic diagram of the experimental system used in this study is shown in Figure 6. OH was produced by titrating H atoms (produced by microwave discharge of traces of H_2 in He) with NO_2 and detected via resonance fluorescence. ClO was produced by the reaction

$$Cl + O_3 \longrightarrow ClO + O_2.$$

where Cl was produced via microwave discharge of Cl_2 in He.

To determine the branching ratio, HCl concentration was to be measured using the millimeter wave absorption technique. HCl concentration was to be monitored at various levels of completion of Reaction (1). The system was to be calibrated for measurement of absolute HCl concentration by flowing known amounts of HCl through the flow tube. $[OH]_o$ would be obtained by titration (i.e., amount NO_2 needed to maximize OH resonance fluorescence signal). By measuring the amount of HCl produced for a given amount of OH consumed, one can calculate k_{1a}/k_1.



MW: Microwave Cavities
PM: Photomultiplier Tube Bandpass Filter Combination
MMI: Millimeter Wave Interferometer
FT: Flow Transducer

Figure 6. Discharge Flow-Microwave F-P Interferometer System.

6. Calculated HCl Concentrations

To determine the molecular concentration of HCl, using the case of the linewidth parameter being 1 MHz/Torr the intensity at ν_0= 625,864 MHz at a pressure of 1 Torr is given as a function of concentration by the relation

$$\gamma = 1.828N \times 10^{-16} \text{ cm}^{-1}$$

This relation can be set equal to the absorption coefficient for the Fabry-Perot interferometer

$$1.828\ N \times 10^{-16} = \frac{2\pi}{\lambda Q_0}\left[\left(\frac{A_0}{A_1}\right)^{\frac{1}{2}} - 1\right]$$

For a resonator $Q_0 = 10^5_7$

$$N = 7.17 \times 10^{12}\left[\left(\frac{A_0}{A_1}\right)^{\frac{1}{2}} - 1\right].$$

Previous work has shown that is possible to measure amplitude ratios to a few parts in 10^3. If we assume a capability to measure the ratio to 5 parts in 10^3 and use a 10 second integration, then

$$N = 5.65 \times 10^9.$$

With increased integration, lower molecular concentrations of HCl can be measured. Concentrations under increased pressure can be measured. The requirements on system sensitivity will be approximately the same for all pressures measured. For stable systems, the increased integration will further enhance our capability to measure concentration.

7. Experimental Investigations

To determine the concentration of HCl in a discharge flow systems, the measurement was to be performed in a semi-confocal interferometer on the $J=0 \longrightarrow 1$ rotational transition at 625,864 MHz. An apparatus was assembled with the power generated by the seventh harmonic of a 89,409.14 MHz klystron. Several different harmonics can be employed to generate the 625 GHz signal if appropriate klystrons are available. Figure 7 shows the apparatus that has been set up for the measurements. A phase-locked x-band signal provides frequency markers for the 89 GHz klystron, the output of which is multiplied in a crossed-waveguide Schottky barrier harmonic generator. The 89 GHz klystron could be phase-locked to the x-band signal and tuned through the resonance frequency, or it can be run freely (unlocked) and swept through the resonator response.

The output of the cross-waveguide harmonic generator (7th harmonic) was applied to the input of the resonator. If video detection were employed at 625 GHz, it would be necessary to use a high-pass filter to cut off all harmonics below the 7th and/or to use a sample of HCl vapor to identify the resonator frequency with a harmonic mixer. For the experiments considered thus far, a superheterodyne receiver has been used with a harmonic mixer configuration. The harmonic mixer is driven by a 312 GHz carcinotron, the frequency of which is not a harmonic of the 89 GHz klystron. As a result, the receiver, on the output of the resonator, not only provides a sensitive detection system, but also serves as a filter against harmonics of the klystron other than the seventh. The receiver output was amplified in a wideband (1-1000 MHz) IF amplifier, further processed in a lock-in amplifier and averaged in a Fabric Tek Signal Averager. The reference for the lock-in amplifier is applied to the reflector of the klystron and can be a square wave (amplitude) modulation or a sine wave (frequency) modulation. The klystron is in addition swept at a 20 Hz rate by the Signal Averager so that the sweeps through resonance are averaged. The reference for the lock-in is at a 1-2 kHz rate. The amplitude modulation will give the resonance shape while the frequency modulation produces the derivative of the resonance.

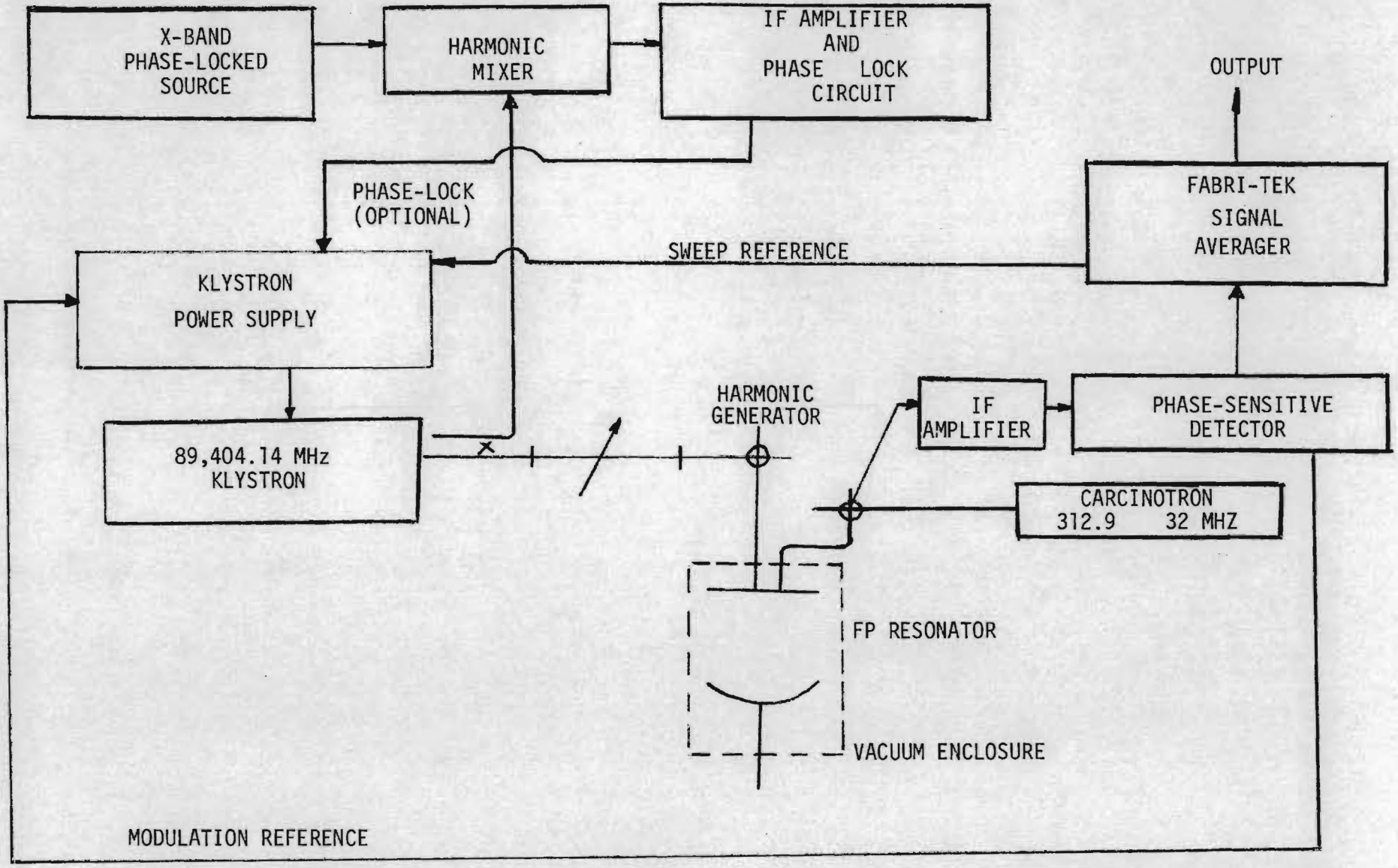


Figure 7. Block diagram of Submillimeter Wave Spectrometer for HCl observation at 625,864 MHz.

The main drawback to completion of the experiments at 625 GHz has been the low power output of the klystron driving the harmonic multipliers. Several klystrons have been tried on the system. It has been possible with a video detector to observe an OCS line at 534,725.11 MHz in a small absorption cell with a fundamental 89,120.86 MHz (6th harmonic) and to detect the 7th harmonic of the 89 GHz signal with the superheterodyne system discussed above. This signal has been observed on a spectrum analyzer. We need sufficient power to put through the resonator and still have sufficient signal strength to observe the HCl absorption.

These experiments will continue at 625 GHz or be performed at 323 GHz on the DCl molecule.

8. Conclusions and Recommendations

From the discussion given in this report, it is seen that, with sufficient excitation power, the concentration of a molecular species in a flow discharge system can be determined. For the case of interest, hydrogen chloride, the experiments can be performed at 625 GHz for $H^{35}Cl$ or at 323 GHz for $D^{35}Cl$. Observation of the isotopic species $H^{37}Cl$ and $D^{37}Cl$, although weaker in concentration, would serve as further confirmation of the experimental technique.

In the experiments discussed above and for which we have made preliminary preparations, we have chosen the $J=0 \rightarrow 1$ transition to be observed mainly since it is the most accessible one for observations with coherent sources. The most intense transition, however, corresponds to the J-value (for pure rotational transitions) given by the root of the equation

$$(2J + 1)(J + 1) = 3kT/hB,$$

which for HCl is J=5. The peak intensity occurs not only from the rotation transition intensity relations, but a further increase over $J=0 \rightarrow 1$ results from the reduction of quadrupole HFS splitting as J increases. This results in an increased contribution to the peak intensity from which the molecular concentration is determined. The higher frequency transitions can be reached by laser/microwave mixing techniques described by Fetterman et al., [9].

Linewidth data are needed for the analysis and this can be performed by techniques employed in this laboratory [10]. Data on the dipole moment of HCl are also required, and techniques are available to acquire this information [11].

The work performed thus far has been by J. J. Gallagher and V. Brady. In addition to the funding of CMA, Georgia Tech contributed an equivalent of $11,500 personal services. Interest in the problem will continue with experiments performed at a reduced rate on in-house funding.

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